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Design of Energetic Ionic Liquids

Jerry A. Boatz

US Air Force Research Laboratory, Space and
Missile Propulsion Division (AFRL/PRSP),
Edwards AFB, CA
jerry.boatz@edwards.af.mil

Greg A. Voth

University of Utah, Salt Lake City, UT
voth@chemistry.chem.utah.edu

Mark S. Gordon

Iowa State University, Ames, IA
mark@si.fi.ameslab.gov

Sharon Hammes-Schiffer

Pennsylvania State University, University
Park, PA
soh3@psu.edu

Abstract

An essential need of the US Air Force is the discovery, development, and fielding of new, energetic materials for advanced chemical propulsion in rocket and missile applications. Some of the key factors driving the requirement for new chemical propellants include: (a) improved performance in terms of increased specific impulse and density, (b) reduced sensitivity to external stimuli such as impact, friction, shock, and electrostatic discharge, and (c) mitigation of environmental and toxicological hazards (and the resulting costs) associated with currently used propellants.

A class of compounds which can potentially meet these requirements is known as ionic Liquids (ILs), which are chemical salts with unusually low melting points. The physical and chemical properties of ILs render them useful for many purposes, most notably as environmentally benign ("green") solvents/reaction media but also as catalysts, electrolytes, etc. From a Department of Defense (DoD) perspective, ILs are being explored as new propellants, explosives, and munitions. The Air Force, in particular, is interested in ILs as potential replacements for currently used monopropellants such as hydrazine—which is carcinogenic, highly toxic, and has relatively modest performance characteristics. In contrast, many ILs have superior densities and specific impulses as well as significantly reduced sensitivity and toxicity characteristics. Furthermore, their properties can be carefully tuned via the choice of the component ions.

The overall objective of the Design of Energetic Ionic Liquids Challenge Project is to address several key technical issues and challenges associated with the

characterization, design, and development of ILs as new monopropellants. Among these, for example, are a fundamental understanding of the instability of ILs, the intrinsic nature of the short- and long-range structure and interactions between the component ions, and identification of the key steps in the initial stages of decomposition and combustion. A hierarchy of computational approaches is employed, including atomistic, high-level quantum chemical methods applied to individual ions and ion clusters, condensed phase atomistic molecular dynamics simulations utilizing polarizable force fields, and mesoscale-level simulations of bulk ionic liquids based upon multiscale coarse graining techniques.

1. Introduction

The design of new high energy density materials (HEDM), which are more efficient, reliable, and environmentally benign than existing rocket propellants, is a high DoD priority. The focus of this effort has been on the development of new propellants and energetic additives, including highly strained hydrocarbons, polynitrogen compounds, and advanced monopropellants. Some of the issues that must be addressed in theoretical efforts to design new HEDM include an assessment of their energy content, their thermodynamic and kinetic stability, and the design of new synthetic routes to proposed new HEDM that have not yet been synthesized.

A specific area of interest to the DoD is the discovery of a suitable replacement for hydrazine, a widely used monopropellant for low-thrust propulsion applications such as orbital maneuvering and satellite stationkeeping. The desire to replace hydrazine is motivated by several

factors. Perhaps the most severe limitation of hydrazine is its carcinogenic nature and extreme respiratory and dermatological toxicity, with correspondingly large costs associated with controlling these environmental and biological hazards. Furthermore, the performance of hydrazine as a monopropellant is rather modest due to its relatively low density and specific impulse compared to a prototypical ionic monopropellant salt such as 4-amino-1,2,4-triazolium dinitramide. The replacement of hydrazine with more energetic, less hazardous energetic monopropellants is clearly needed.

A specific type of HEDM of current interest is derived from a broad class of compounds known generically as ionic liquids (ILs), which are chemical salts with unusually low melting points; e.g., below 100° C. The general interest in ILs has focused mainly on their use as environmentally benign (“green”) solvents for a wide range of chemical reactions. Some of the properties of ILs which make them attractive as solvents include their low vapor pressure, large liquid ranges, and thermal stability. The interest in ILs as new monopropellants stems from several factors. For example, the properties of ILs, including their energy content, can be “tuned” through a judicious choice of component ions and their substituents. Furthermore, the virtually nonexistent vapor pressure of ILs greatly reduces the environmental and biological hazards due to respiratory and dermatological toxicity. Finally, the densities of ILs generally are significantly greater than those of conventional liquid monopropellants such as hydrazine.

Although there have been extensive experimental studies of chemical reactions in ILs, little has been done in the area of characterization of the fundamental chemical and physical properties of ILs. In particular, one of the most pressing needs in the broader area of IL development, and particularly in the design of energetic ILs, is the application of robust theoretical methods for the reliable prediction of IL heats of formation, synthesis routes, phase transitions, ion conformations, thermal stabilities, densities, and viscosities. The focus of this study is on the characterization, design, and synthesis of the next generation of monopropellants for rocket propulsion applications.

2. Computational Methods

An integrated approach utilizing multiple computational methods is used to predict and characterize the intrinsic and bulk properties of energetic ionic liquids.

At the molecular level, highly accurate electronic structure methods are used to predict the fundamental properties of the ionic liquid components, including molecular structures, charge delocalization, heats of formation, and proton transfer reaction pathways and barriers. Geometries, electronic structures, and properties (including heats of formation) of the component ions are predicted using second-order perturbation theory (MP2, also known as MBPT(2)^[1]), density functional theory (DFT)^[2], and the “Gaussian-N” (GN)^[3] methods. The Nuclear-Electronic Orbital (NEO)^[4] approach is used for capturing the quantum dynamical effects of hydrogen bonding and proton transfer. In addition, the complex spectrum of ionic liquid physical properties requires utilization of polarizable force fields in condensed phase simulations in order to obtain reliable predictions of many key bulk properties.

3. Results and Discussion

A systematic study^[5] has been carried out on a series of substituted pentazole-based cations, including predictions of the molecular structures, heats of formation and extent of electron delocalization. The 1H,3R isomers were found to be approximately 20 kcal/mol more stable than the corresponding 1H,2R structures. It was also determined that the 1H,1R isomers are all unstable, spontaneously leading to formation of one or more nitrogen molecules and a cationic fragment. The contributions of the primary resonance structures in the parent 1H,2H and 1H,3H cations were found to be roughly equal, indicating that the excess positive charge is highly delocalized in the ring. The small geometry changes in the rings in the derivative cations suggests that substitution does not significantly change the degree of charge delocalization. It appears that substitution will not hinder the ability of these cations to form ionic liquids.

Heats of formation: The gas-phase heats of formation have been computed using a combination of G2 theory^[3] and isodesmic reactions^[6], as described in detail elsewhere^[5], and are summarized in Table 1. The heat of formation of the un-substituted 1,3 (1,2) cation is 286.5 (303.9) kcal/mol. Most substituents increase this value, the exceptions being -CH₃, -OH, -CH₂NO₂, and -OCH₃. The largest increases in heat of formation occurs for -CN and -N₃. These results are similar to those found in previous studies of substituted triazolium^[7] and tetrazolium^[8] cations.

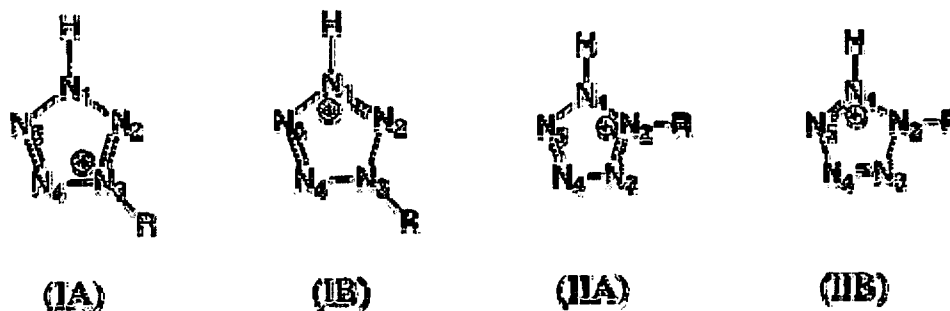


Table 1. Heats of formation at 298K for gas-phase monosubstituted 1h,3r- and 1h,2r-pentazole cations^a

R	1H, 3R isomers		1H,2R isomers	
	ΔH_f° (kcal/mol)	ΔH_f° (kcal/g)	ΔH_f° (kcal/mol)	ΔH_f° (kcal/mol)
H	285.6	4.0	303.9	4.2
F	307.6	3.4	328.2	3.6
CH ₃	268.0	3.1	284.5	3.3
CN	358.3	3.7	376.8	3.9
NH ₂	301.6	3.5	317.7	3.7
OH	282.8	3.2	300.3	3.4
CH ₂ NO ₂	278.3	2.1	295.6	2.2
N ₃	392.3	3.5	407.9	3.6
NF ₂	315.6	2.6	333.7	2.7
C ₂ H ₃	294.0	3.0	310.5	3.2
OCH ₃	277.2	2.7	293.0	2.9

Table 2. Activation energies (e_a) for the decomposition of protonated pentazole to form the corresponding azidinium cations and N₂ (including zero-point energy correction, in kcal/mol)^a

	1,3-Isomer	1,2-Isomer	
	E_a	E_{a1}	E_{a2}
	CR-CCSD(T)	CR-CCSD(T)	CR-CCSD(T)
H	28.2	30.9	46.1
F	24.2	22.1	37.5
CH ₃	28.8	35.6	53.9
CN	22.4	22.3	39.3
NH ₂	22.6	24.6	57.8
OH	22.0	24.6	40.2
CH ₂ NO ₂	26.8	30.7	13.6
N ₃	20.2	25.2	6.4
NF ₂	23.3	23.4	39.3
C ₂ H ₃	26.8	31.1	50.8
OCH ₃	21.9	26.8	16.0

^aSubscripts 1 and 2 label the first and second activation energies, respectively, for the 1,2-isomer. E_{a2} is calculated relative to the final decomposition products.

Cation Transition States and Decomposition

Products: The 1H,3R isomers are found to decompose to N₂ + [HN₃R]⁺ via a single-step mechanism. The energy barriers vary with substituent from 20 to 29 kcal/mol at

the CR-CCSD(T) level of theory, as shown in Table 2. In contrast, the decomposition mechanisms of the 1H,2R isomers are more complex, involving two-step processes that likewise result in formation of N₂ + [HN₃R]⁺. The

only exception is for $R=CH_2NO_2$, in which case the 1H,2R decomposition products are $N_2 + HONO + [H_2CN_3]^+$. The barriers for the first step of the 1H,2R decomposition pathways range from 22 to 36 kcal/mol as a function of substituent, whereas the barriers for the second step range from 6 ($R=N_3$) to 58 ($R=NH_2$) kcal/mol, at the CR-CCSD(T) level (see Table 2).

Proton Transfer: When a cation is paired with an oxygen-rich anion, a single gas phase ion pair is not generally found to be stable. A proton transfers with little or no barrier from the cation to the anion to form a neutral pair, suggesting that proton transfer is a key step in the decomposition of protonated pentazoles. The largest barrier found in this study was ~6 kcal/mol, at the MP2/6-311G(d,p) level of theory, for the 1H,3H pentazolium-dinitramide pair. The 1H,3H cation paired with perchlorate (nitrate) has a proton transfer barrier of 2.7 (3.0) kcal/mol.

[Emim⁺][Im⁻] Ion Clusters: Ionic liquids such as 1-ethyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl) imide ([Emim⁺][Im⁻]) show great promise as advanced working fluids in electric propulsion applications. In order to assess and tune the performance of these types of working fluids, it is necessary to characterize the exhaust plume, which contains a distribution of clusters such as [Emim⁺]_m[Im⁻]_{m±1}; i.e., containing either an excess cation or anion. The gas-phase structures, harmonic vibrational frequencies, binding energies, and internal thermal energy distributions of a series of ion clusters [Emim⁺]_m[Im⁻]_{m±1} ($m=1-3$) were computed using the hybrid B3LYP density functional and the 6-311++G(d,p) basis set. The computed structures and scaled harmonic frequencies were used to calculate the temperature-dependent internal thermal energy distributions, as illustrated in Figure 1 for the [Emim⁺][Emim-Im] and [Im⁻][Emim-Im] ion clusters, and compared to experimental mass spectrometric measurements of ion cluster abundances. The shift in the theoretical internal energy distributions to higher energies as a function of temperature suggest that the population of these ion clusters in the gas phase should decrease with increasing temperature. In the case of the [Im⁻][Emim-Im] cluster, however, the experimental ion mass spectra show the abundance of the [Im⁻][Emim-Im] cluster has a minimal temperature dependence. This suggests that additional factors such as rapid dissociation of larger clusters to form evaporatively cooled [Im⁻][Emim-Im] clusters may be important.

Bulk Properties: An electronically polarizable force field^[9] for ionic liquids (IL) has been developed by the Voth group, based on Thole's smearing dipole model^[10], in which each atomic site is treated as a polarizability center and the anisotropic molecular polarizability may be reproduced through the interaction among the atomic sites. In molecular dynamics (MD) simulations, the

induced dipole is propagated by the extended Lagrangian method^[11].

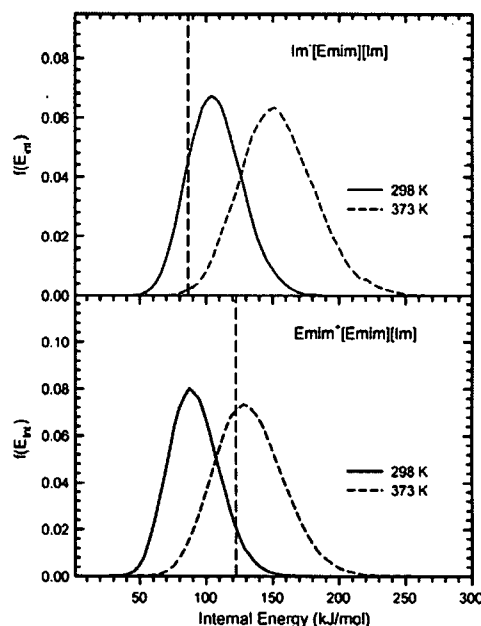


Figure 1. Calculated thermal internal energy distributions at 298 and 373K for $Im-[Emim][Im]$ (top) and $Emim+[Emim][Im]$ (bottom). The vertical dashed lines represent the dissociation limits of the respective cluster ions.

Our molecular dynamics study^[12] of 1-hydroxyethyl-4-amino-1,2,4-triazolium nitrate (HEATN) have identified a glass transition temperature region around 275K, in agreement with experiment^[13]. Various other physical properties of liquid state were intensively studied at 400K. The viscosity was fitted as 64.25 and 38.21 c.p., by the nonpolarizable and polarizable models^[9], respectively, as shown in Figure 2. A study of structural properties of liquid/vacuum interface shows that there is vanishing layering at the interface, in accordance with the poor ion packing. The calculated surface tension is 68.37 ± 2.98 mN/m and 93.91 ± 2.43 mN/m, for the nonpolarizable and polarizable model, respectively^[12].

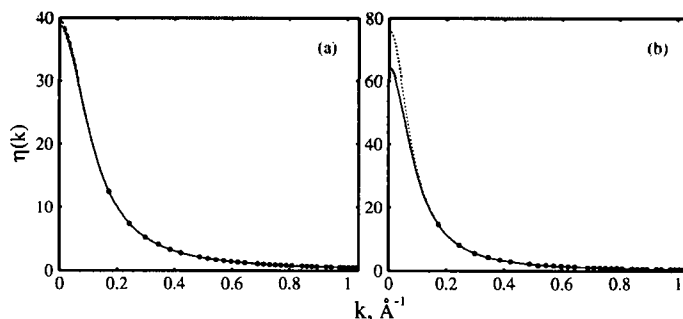


Figure 2. Calculated viscosity curves of HEATN at T=400K, using (a) polarizable and (b) nonpolarizable force fields

Nanostructural Organization in Ionic Liquid/Water Mixtures:

Atomistic molecular dynamics simulations utilizing the standard Amber force field^[15] have been performed on a series of mixtures of 1-octyl-3-methylimidazolium nitrate ionic liquid and water. The nitrate anion, the aromatic ring of the cation, and the single methyl group bonded to the ring were designated the polar groups and are shown as red in Figure 3. The whole alkyl chain was defined as the nonpolar group and colored yellow, and the water molecules are shown as dark blue. These simulations show that, within the range of water contents examined, polar networks, water networks and micelles possess an approximately invariant characteristic length at around 20 Å. Furthermore, as the amount of water increases, the polar network is continuously broken up (screened) by the intruding water, while the structural organization of the water network and the micelle exhibits a *turnover*, as shown in Figure 4. The turnover of structural organization of micelles results from the persistent competition between the hydrophobic interactions of the nonpolar groups and the break up of the charged polar network with increasing water content, while the turnover of the water network results from the competition between the water-water and water-anion interactions^[14].

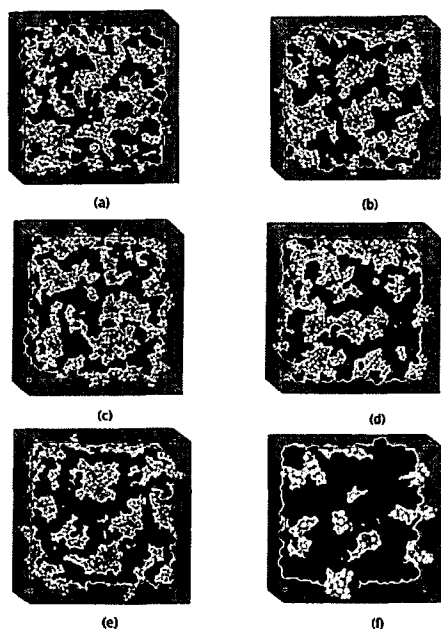


Figure 3. Snapshots of six selected simulation cells, taken from the MD trajectory data. The polar groups, nonpolar groups, and water are colored red, yellow, and dark blue, respectively. (a) Dry IL sample, (b) mixture with water of 20% mole fraction, (c) 50% mole fraction, (d) 75% mole fraction, (e) 80% mole fraction, (f) 95.2% mole fraction.

Hydrophobic Behavior of Non-polar Molecules in Ionic Liquids:

Figure 4 shows the aggregation of methane molecules in 1-butyl-3-methylimidazolium chloride ionic liquid (BMIM⁺/CL⁻). The chloride anion, the aromatic ring of the cation, and the single methyl group bonded to the ring were designated the polar groups and are shown as red. The whole butyl chain was defined as the nonpolar group and colored yellow, and the methane molecules are shown as dark blue. The aggregation of nonpolar molecules decreases with increasing symmetries of the anions, or equivalently, decreases with decreasing strength of electrostatic attraction between polar head/anion groups. For a given anion, the aggregation decreases with increasing length of the side chain. A comparison between methane and butane shows that methane molecules have much stronger aggregation tendency than butane. The above results^[16], together with the polar/nonpolar phase separation in pure ionic liquids, can be explained by a unified entropic origin^[17].

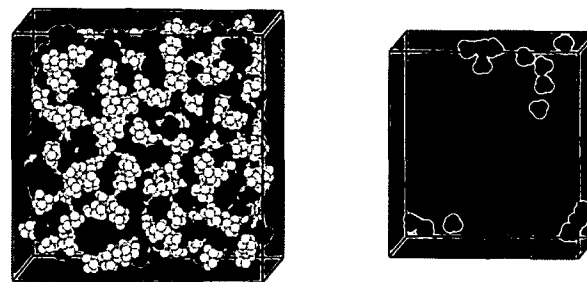


Figure 4. Snapshot of BMIM⁺/CL⁻ simulation cell, taken from the MD trajectory data. The polar groups, nonpolar groups, and methane are colored red, yellow, and dark blue, respectively. In the panel on the right, the polar and nonpolar groups have been removed in order to reveal the positions of all the methane molecules.

4. Summary and Conclusions

The geometries, electronic structures, and heats of formation of a series of substituted pentazole-based cations have been predicted using quantum chemical methods. The 1H,3R isomers are found to be approximately 20 kcal/mol more stable than 1H,2R, whereas all of the 1H,1R spontaneously decompose to form one or more nitrogen molecules and a fragment cation. Electron-donating substituents such as methyl, hydroxyl, methoxy, and nitromethyl groups lower the heat of formation relative to the unsubstituted cation. The opposite behavior is observed for electron-withdrawing groups, with cyano (-CN) and azido (-N₃) groups yielding the largest increases in the heat of formation. The 1H,3R isomers decompose to form N₂ + [HN-₃R]⁺ by a one-step mechanism, whereas the 1H,2R isomer decomposition involves two steps connected by an open-ring

intermediate. The gas-phase proton transfer reactions of the 1H,2R/1H,3R cations with dinitramide, perchlorate, and nitrate anions have been calculated. At the MP2/6-311++G(d,p) level of theory, the energy barriers for these reactions are found to be small (~ 6 kcal/mol) or nonexistent, suggesting that proton transfer is a key step in the decomposition of these ionic liquids.

The structures, harmonic vibrational frequencies, binding energies, and internal thermal energy distributions of gas-phase ion clusters of the 1-ethyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide ionic liquid have been predicted using density functional theory (B3LYP/6-311++G(d,p)). The calculated internal energy distributions predict a temperature dependence of the population of the [Im]⁺[Emim-Im] ion clusters, but not seen in mass spectrometric experiments. This suggests that additional effects such as rapid dissociation of larger clusters to form evaporatively cooled [Im]⁺[Emim-Im] clusters may be important.

Classical molecular dynamics simulations of HEATN predict the presence of a glass transition at a temperature of about 275K, in agreement with experiment. Utilization of a polarizable versus a nonpolarizable force field resulted in significant differences in predicted transport properties such as self-diffusion coefficients and shear viscosity. Simulations of 1-octyl-3-methylimidazolium nitrate ionic liquid/water mixtures show that as the amount of water increases, the polar network is continuously disrupted by the intruding water, while the structural organization of the water network and the micelle exhibits a "turnover." In contrast, simulations of methane in [BMIM]⁺[Cl]⁻ show that aggregation of nonpolar molecules decreases with increasing symmetries of the anions, or equivalently, decreases with decreasing strength of electrostatic attraction between polar head/anion groups.

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